COAL LIQUEFACTION UNDER HIGH-MASS FLUX AND SHORT-RESIDENCE TIME CONDITIONS*

Carl L. Oberg, Arthur Y. Falk, George A. Hood, and James A. Gray

Rockwell International/Rocketdyne Division
6633 Canoga Avenue, Canoga Park, CA 91304

INTRODUCTION

This paper describes progress made during the first year of a program directed toward developing and evaluating a concept for reacting pulverized coal with heated hydrogen to form hydrocarbon liquids suitable for conversion to fuels or for use as chemical feed stocks. The basic concept of the process is that high liquid yields are favored by rapid mixing, reaction, and subsequent quenching of the reacting mixture. The pulverized coal is being injected into the reactor by dense-phase transport, with a minimum amount of carrier gas required. A rocket engine-type injector is being used to rapidly and uniformly mix the coal with hydrogen that has been heated to 1200 to 2000 F. Reaction times of 10 to 1000 milliseconds at temperatures of 1500 to 1900 F and pressures of 500 to 1500 psi are being explored. The concept is being evaluated with a simple water-spray quench system.

The initial effort was directed toward cold-flow testing to develop suitable methods of transport, injection, and mixing of the pulverized coal. Subsequently, reactor testing was begun at a nominal coal flowrate of 0.2 tons per hour (tph). Preparations are also being made for testing at 1 tph.

COLD-FLOW TESTING

The purpose of the cold-flow testing was to develop effective means of feeding the pulverized coal into a reactor and suitably mixing this coal with incoming hydrogen. Dense-phase transport of the coal was chosen to minimize the gas requirement for feeding the coal and, thus, maximize the gas available for heating, because the process heat is supplied by heating the incoming hydrogen. Further, cold-flow mixing tests were made to allow selection of injector configurations and operating conditions that would produce a high level of mixing uniformity. This high mixing uniformity is needed to ensure that the coal particles are exposed to a uniform reaction environment and reaction time during their brief residence time in the reactor. Poor mixing would tend to cause some of the particles to be insufficiently reacted, thereby producing a poor yield, and others to react for too long a period of time, with attendant cracking of the oils into gases. This mixing optimization was accomplished by adapting mixing characterization techniques that are used for performance optimization of rocket engine injectors.

TRANSPORT AND FEEDING TESTS

Cold-flow tests were made with two simple pressurized feeders to evaluate the dense-phase feeding and transport characteristics of the pulverized coal. One of these feeders was made from a 4-inch-diameter Pyrex pipe 4 feet long and the second was made from a 10-inch steel pipe 17 feet long. A 30-degree included-angle cone was used in the bottom of each. Pulverized coal fed from each feeder through a ball valve and through steel tubing into a catch vessel. No fluidizing gas was provided other

*Program funded by ERDA Fossil Energy, Division of Coal conversion and Utilization (Contract E(49-18)-2044)

than that associated with pressuring the feeder. The transport gas requirement was inferred from the rate of gas flow to the feeder during the flow of solids. Pressures were measured at the top of the feeder and at several points in the feed line.

Tests were made with two coal particle sizes--170 micron and 54 micron mass median (27 and 74 percent through a 200-mesh screen). In most cases, nitrogen was used as a carrier gas but tests were also made with helium and carbon dioxide to assess density effects. The coal was fed through 1/2-, 3/8-, and 1/4-inch tubing (inside diameters of 0.402, 0.277, and 0.180 inch, respectively).

Typical pressure gradient results are shown in Fig. 1. An approximate minimum pressure gradient is shown below which the coal would not flow. For each particle size, the pressure gradient results tended to fall along a single line irrespective of tube diameter. The coarser coal, which was used repeatedly because of a limited supply, produced an increased pressure gradient with increased usage, although the results still exhibited the same dependence on solids mass flux. The pressure gradient was unaffected by the substitution of helium or carbon dioxide for nitrogen as the transport gas. The difference in pressures between that measured in the feeder and that measured near the upstream end of the feed line exhibited a similar dependence, varying from 1.6 to 14 psi at solid mass fluxes of 400 and 1500 lbm/ft-sec, respectively.

The transport gas requirement is shown in Fig. 2. The results indicate that the coal is leaving the feeder at near its static bulk density and only the gas carried in the interstices of the particles is required for transport.

The dispersed solids density was measured by simultaneously closing two ball valves in the line to trap the amount of solids being carried. For the 170 micron coal, this density exhibited a power law dependence on solids mass flux, varying from 50 to 30 lbm/ft^3 at 150 and 700 lbm/ft^2-sec for each carrier gas.

Results from this testing have shown that pulverized coal can be effectively fed from a simple pressurized feeder. The dense-phase flow is smooth and reproducible. Flowrates from ~0.1 to 1.0 lbm/sec were readily obtained. Flowrates ~10 lbm/sec were obtained with another pressurized feeder, used for loading the 10-inch pipe feeder.

COLD-FLOW MIXING TESTS

Cold-flow tests were also made to define coal/gas injector configurations and operating conditions which will give rapid and uniform mixing. Because techniques have been developed for achieving and characterizing injector mixing for liquid-propellant rocket engines, these techniques were adapted for the coal/gas case. Furthermore, injector configurations known to give high levels of mixing in rocket engines were considered primary candidates for the coal/gas case.

For this testing, nitrogen was chosen as a simulant for the heated hydrogen in the reactor. Both the gas injection velocity and density were modeled in the cold-flow case. The pressure in the cold-flow chamber was chosen to give a gas density corresponding to that of the hydrogen at injection conditions. To model hydrogen at 1000 psia and 1500 F, the nitrogen pressure should be 19.1 psia. Consequently, the use of nitrogen allowed the tests to be made at nearly atmosphere conditions.

A two-phase flow probe was used to characterize the flowfield created by the coal/gas injection. Similar probes have been used extensively to characterize gas/liquid

injection for rocket injectors (e.g., Ref. 1 and 2). These probes have been developed from that originally used by Dussourd and Shapiro (Ref. 3).

The cold-flow mixing tests were made with a single injection element in the cold-flow chambers. A secondary flow of gas was also used in the chamber to suppress recirculation. Data from the probe tests were analyzed to calculate the local mass fluxes of a gas and coal. The local mass flux values were numerically integrated to obtain collection efficiencies by comparison with measured injection flowrates.

The resultant mass flux distributions were plotted for qualitative assessment; also, a mixing efficiency was calculated. The mixing efficiency used was one developed for rocket engine injector characterization by Rupe (Ref. 4). This mixing efficiency is usually expressed as

$$E_m = 1 - \sum_{r_i<R} MF_i \left(\frac{R-r_i}{R}\right) - \sum_{r_i>R} MF_i \left(\frac{R-r_i}{R-1}\right) \qquad 1)$$

where $MF_i = \frac{(m_c + m_g)_i}{\sum (m_c + m_g)_i}$ and $R = \frac{\sum m_{ci}}{\sum (M_c + m_g)_i}$ and $r_i = \frac{m_{ci}}{m_{ci} + m_{gi}}$ and m_{ci}, m_{gi}

are the local mass flowrates of coal and gas, respectively, in the i^{th} steamtube. A relatively simple interpretation of Eq. 1 can be obtained by recognizing that the terms in parenthesis in the equation represent local deficiencies of the fractional mass fluxes. The flowfield data were numerically integrated to obtain the mixing efficiencies.

Two coal/gas injector configurations were chosen for cold-flow evaluation: a concentric tube configuration and a 4-on-1 impinging configuration. Both of these yield high mixing efficiency in rocket applications. Further, they were not expected to result in substantial impingement of coal on the walls. The concentric tube element involves coaxial flow of the two streams with coal in the central tube and gas flowing in the annulus. The 4-on-1 element involves impingment of four gas streams on a central coal stream. The dimensions of the injection elements were also selected on the basis of rocket engine experience.

Results from the cold-flow mixing tests are summarized in Fig. 3 and 4. High levels of mixing efficiency have been obtained, with both types of elements. In rocket engines, mixing efficiencies greater than 80 to 90 percent lead to very high combustion efficiencies (>95 percent).

The mixing results obtained with the concetric tube element exhibit different trends from those obtained with gas/liquid injection element, probably because of differences in the shear interaction in the element. Conversely, the coal/gas 4-on-1 injector exhibits qualitatively similar characteristics to a gas/liquid or liquid/liquid injector. Optimum mixing was obtained with two different diameter ratios, although in each case, the mixing on only one side of the optimum has been defined.

These two results may be used to obtain a diameter ratio dependence as:

$$\left[(\rho u^2)_g/(\rho u^2)_c\right]_{optimum} = 12.6\ (D_g/D_c)^{2.1} \qquad 2)$$

or

$$\frac{D_g}{D_c} = \left[\frac{1}{12.6\ (4^2)} \left(\frac{\dot{m}_g}{\dot{m}_c}\right)^2 \frac{\rho_{ds}}{\rho_g}\right]^{1/6.1} \qquad 3)$$

High levels of mixing have been demonstrated with both the concentric-tube and 4-on-1 element configurations. The highest levels of mixing were obtained with the 4-on-1 configuration, although either type appears suitable on the basis of mixing for reactor testing. Furthermore, the ability to use a two-phase flow probe to characterize coal/gas mixing has been demonstrated.

REACTOR TESTING

Reactor testing currently under way is directed toward evaluation and development of a reactor based on the short-residence time concept. The reactors are being designed to promote rapid mixing (based on the cold-flow results) and to obtain relatively high gas velocities, to promote interaction (mass transfer and reaction) of the gas with the particle. The hydrogen is being partially heated by indirect heating and by partial combustion with oxygen as necessary to supply the required process heat. The reactor is being operated with high internal wall temperatures to minimize a tendency for adhesion of the partially reacted coal particles on the wall. The amount of hydrogen fed is being kept as low as practical because of the recycle implication for a complete process. A simple water-spray quench system is being used.

Reactor testing was begun with a system capable of feeding 35 lbm of coal at a planned flowrate of ~0.1 lbm/sec (~0.2 tph). The 0.2 tph reactor assembly is illustrated in Fig. 5 and a schematic flow diagram of the test system is shown in Fig. 6. The reaction chamber for most tests was a 1-1/2-inch-diameter, 0.049-inch-wall stainless steel (type 321) tube, 36 inches long. This reaction chamber is contained within an insulated pressure vessel made from 8-inch pipe. Coal is fed in dense phase to the reactor from a pressurized feeder of the type used during the cold-flow testing. The feeder is a 6-inch diameter vessel with a conical (15-degree half angle) exit. Reaction products pass from the reaction chamber into a quench section, which has a set of water spray nozzles, and into a char receiver. The hydrogen is heated in a 260-inch-long coiled tube that is heated by passing an electric current through the tube. Up to 150 killowatts of power is supplied to this tube by seven motor-generator sets. Nearly all of this power is transferred to the hydrogen as heat.

Two types of inejctors have been used: a concentric tube and a 4-on-1 configuration. The 4-on-1 injector configuration is shown in Fig. 7. The body of this injector is made from a 1-1/2-inch tube fitting tee. The heated hydrogen enters the injector from the side, flows around the insulated coal feed tube, and through four injection orifices. The four hydrogen streams impinge with a 30-degree half angle at a point 0.400-inch from the injector face. Also included are four oxygen injection orifices which also impinge with an angle of 30 degrees but at a distance of 0.700 inch from the injector face.

Initial testing was directed toward solving operational problems with the system. The initial tests were made with the concentric tube injector and without oxygen addition. The reactor temperature was found to be lower than anticipated during these tests. The reaction process appeared to exhibit thermally neutral character whereas exothermic character was anticipated. Hydrogen-to-coal flowrate ratios near 0.36 were required to obtain a reactor outlet temperature 1100 F. A reactor outlet temperature ~1500 to 1800 F was believed to be needed for high conversions. Further, it was found that the char in the reactor tended to agglomerate and adhere to the walls of the reactor. The latter problem was believed due to a low reactor wall temperature, which was $\leq$1000 F during initial tests. Feldmann et al. (Ref. 5) report that wall temperatures of 1340 to 1470 F were required in the Hydrane reactor to avoid wall adhesion. The system and operating procedures were modified to minimize heat losses from the reactor tube and, also electric wall heaters were tried. However, the wall temperatures were not increased sufficiently to eliminate the wall adhesion problem. Therefore, the system was modified to allow the addition of oxygen to raise the temperatures by partial combustion.

Two methods of oxygen addition were tried: (1) injection in a small combustor upstream from the injector, and (2) injection directly into the reactor. Relatively small amounts of oxygen are required to increase the gas temperature to near 2000 F. Both methods were successful, although some difficulties were encountered with overheating the injectors and preburners with the preburner approach. Agglomeration was largely eliminated for reactor temperatures greater than ~1600 F and reactor plugging due to wall adhesion did not occur with reactor temperatures above ~1500 F.

A series of tests was made to assess the effects of reactor temperature, location of oxygen addition, residence time, and velocity.

The raw char gas samples, and aqueous samples from the tests have been analyzed to determine the composition of the products and to allow calculation of material balances. The gas samples were analyzed by gas chromatography for N_2, H_2, O_2, CO, CO_2, and C_1 to C_4 hydrocarbons. A gas chromatographic analysis is used also for benzene, toluene, and xylene. The latter procedure was confirmed by mass spectrometric analysis. Also, the sample bottles are washed with a solvent to remove tar-like materials.

Aqueous samples from the cyclone and secondary separators and the water removed from the char receiver have been analyzed for carbon content with a total carbon analyzer.

The raw char samples are weighed, air dried, and reweighed after which a portion of the sample is dried in an oven at 221 F for 1 hour. A portion of the air-dried sample is sent to an outside laboratory for proximate and ultimate analyses. Also, an analytical benzene extraction, employing a Soxhlet apparatus, is used to determine an extractable fraction. Most of the extractions have been made with material dried at 221 F for 1 hour. An ash analysis is also made.

Typical results from the 0.2 tph testing are shown in Tables 1 through 3, which summarize the test conditions and product composition from four tests made with the 4-on-1 injector.

Carbon conversion results from the 0.2 tph testing are shown in Fig. 8, which shows overall and gas conversions. Results are shown from tests made with a basic reactor size of 1.402 inch diameter x 36 inch long and also with 0.995 inch diameter x 36 inch, 1.995 inch diameter x 36 inch and 1.402 diameter x 18 inch reactors. Thus, the reactor residence time was increased and decreased by a factor of 2.0 from the base case. The overall conversion has been calculated with the ash in the coal being used as a tracer. In most cases the ash recovery was in the range of 90 to 100 percent. The overall conversions appear to vary most strongly with temperature and residence time, while changes in the location of oxygen addition (preburner or reactor) and injector (concentric tube or 4-on-1) had relatively small effects. The effect on conversion to gas of changing the location of oxygen addition was significant. The increase in gas formed with oxygen addition in the reactor appears to result from oxidation of liquid products.

Carbon conversion to liquids is shown in Fig. 9. Not all of the carbon was recovered during many of the tests. This lost material is belived to be liquid, probably a mist of small droplets not removed by the cyclone separator and settling tank. Some tarry material was recovered from the gas sample bottles but the accuracy of that sample is not sufficient for it to be used to account for the carbon deficit. Tar quantities ranging from a few milligrams to a few grams have been obtained while samples in the middle of this range would account for the loss. The carbon fraction corresponding to the liquid obtained by benzene extraction of the char and tar removed from the separators is shown in Fig. 9 along the fraction inferred by difference. The carbon deficit is shown in Fig. 10.

Current effort is directed toward improving the carbon recovery and preparation for reactor testing at 1 tph.

CONCLUSIONS

Results from the testing are regarded as highly significant and encouraging. Effective methods of feeding the coal and of injection and mixing of the hydrogen and coal have been developed. Significant progress has been made on developing the desired reactor process and feasibility has been demonstrated. For comparable flowrates, the size of this reactor is several orders of magnitude smaller than some of the other liquefaction reactors being developed.

The test results indicate high overall conversion, approaching that required for a balanced plant operation. Liquid yields also appear high, although the lack of total recovery leaves some uncertainty.

REFERENCES

1. Burick, R. J.: Space Storable Propellant Performance Program Coaxial Injector Characterization, Contract NAS3-12051, NASA CR-120936, Rocketdyne Division Rockwell International, Canoga Park, California, October 1972.

2. McHale, R. M.: Noncircular Orifice Holes and Advanced Fabrication Techniques for Liquid Rocket Injectors - Final Report Phases III and IV, R-9270, Rocketdyne Division, Rockwell International, Canoga Park, California, May 1974.

3. Dussourd, F. L. and A. H. Shapiro: "A Deceleration Probe for Measuring Stagnation Pressure and Velocity of a Particle Laden Gas Stream," Jet Propulsion, January 1958, pp. 24-34.

4. Rupe, H. J.: A Correlation Between the Dynamic Properties of a Pair of Impinging Streams and the Uniformity of Mixture-Ratio Distribution in the Resulting Spray, Progress Report No. 20-209, Jet Propulsion Laboratory, Pasadena, California, 28 March 1956.

5. Feldmann, H. F., J. A. Mima, and P. M. Yavorsky: "Pressurized Hydrogasification of Raw Coal in a Dilute-Phase Reactor," Coal Gasification, edited by L. G. Massey, Advances in Chemistry Series No. 131, American Chemical Society, Washington, D.C., 1974, pp 108-125.

TABLE 1. TEST CONDITIONS FOR TYPICAL TESTS

Test Number	Total Coal, lbm	Duration, seconds	Flowrates, lbm/sec			Average Temperatures, F			Injector
			Coal	H_2	O_2	Wall	Reactor	Calculated Reactor	
23	19.7	234	0.084	0.0383	0.0226	1780	1780	1830	4-on-1
24	15.6	210	0.074	0.0380	0.0230	1820	1700	1920	↓
25	17.0	155	0.110	0.0372	0.0149	1430	1400	1590	
26	19.2	240	0.080	0.0386	0.0196	1550	1500	1770	

NOTES: (1) Tests 23, 24, and 26 were made with oxygen injection in the reactor.
(2) Test 25 was made with oxygen injection in the preburner.
(3) Calculated reactor temperatures correspond to mixing with no heat of reaction.

TABLE 2. COMPOSITION OF COAL, CHAR AND LIQUID PRODUCT FROM TYPICAL TESTS

Constituent	Composition, percentage by weight					
	Coal	Raw Char				Benzene Extractable Material
		Test 23	Test 24	Test 25	Test 26	
Moisture	2.05	2.83	5.96	7.49	5.17	
Ash	10.56	18.54	18.95	14.71	15.89	
Carbon	69.25	69.97	67.15	67.94	71.01	85.70
Hydrogen	4.87	2.82	2.64	2.78	2.66	5.67
Nitrogen	1.46	0.58	0.71	1.38	0.95	1.08
Chlorine	0.01	0.01	0.01	0.02	0.01	
Sulfur	4.26	3.28	3.11	3.16	2.65	
Oxygen (Diff.)	7.54	1.97	1.47	2.52	1.66	
Benzene Extractable Fraction	0.5	15.5	9.9	18.3	23.2	

TABLE 3. COMPOSITION OF PRODUCT GAS FROM TYPICAL TESTS

Component	Mole Fraction, percent			
	Test 23	Test 24	Test 25	Test 26
N_2	2.6	0.9	1.3	2.5
H_2	89.4	91	93	89
CO	4.7	3.4	0.3	1.8
CO_2	0.2	0.2	0.1	0.1
CH_4	2.2	4.0	1.6	1.1
C_2H_4	-	<0.1	<0.1	<0.1
C_2H_6	0.2	0.1	0.4	0.2
C_3H_8	-	-	<0.1	-
C_4H_{10}	-	-	-	-
Benzene	$7.7(10^{-4})$	$7.3(10^{-4})$	$2.5(10^{-4})$	$5.1(10^{-4})$
Toluene	$3.8(10^{-5})$	$1.3(10^{-5})$	$1.3(10^{-4})$	$4.8(10^{-5})$
Xylene			$2.8(10^{-5})$	$1.2(10^{-6})$

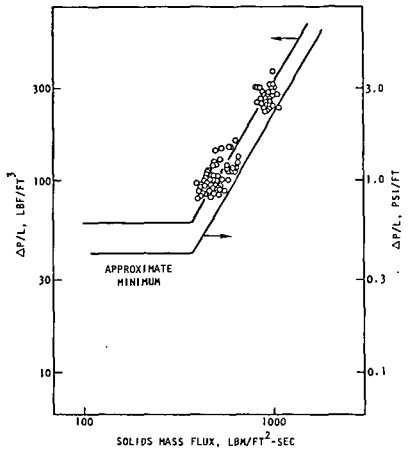

Figure 1. Measured Transport Line Pressure Gradient Obtained From Mixing Test Facility

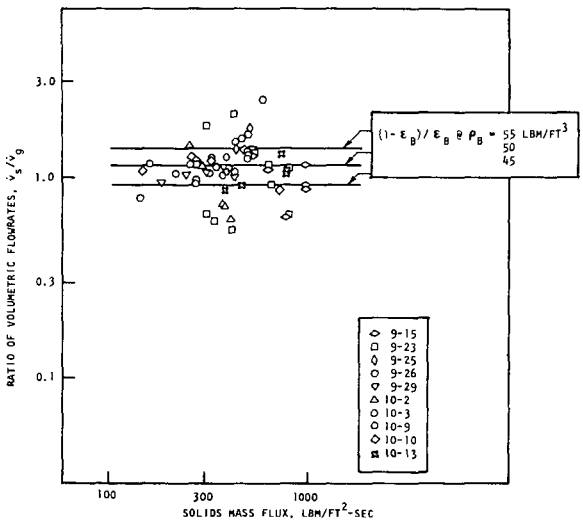

Figure 2. Ratio of Solid-to-Gas Volumetric Flowrates Obtained From Transparent Feeder Data

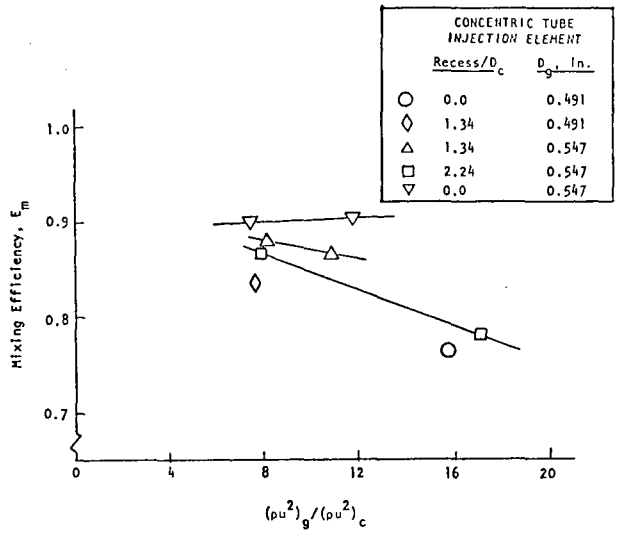

Figure 3. Cold-Flow Mixing Results From Concentric Tube Injection Elements

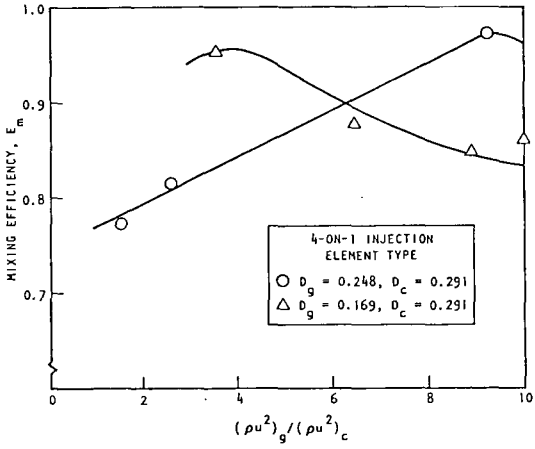

Figure 4. Cold-Flow Mixing Results From 4-on-1 Injection Elements

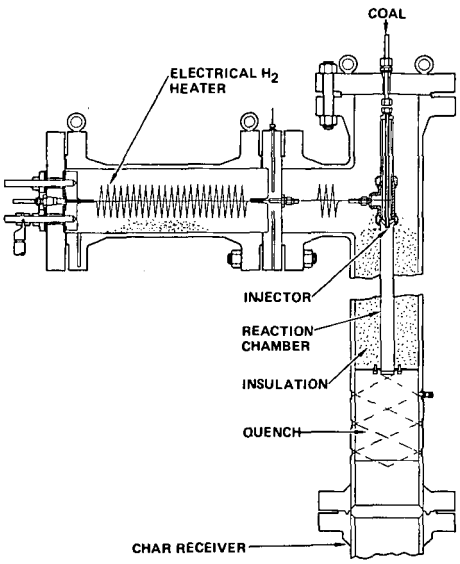

Figure 5. Schematic Diagram of 0.2-tph Reactor Assembly

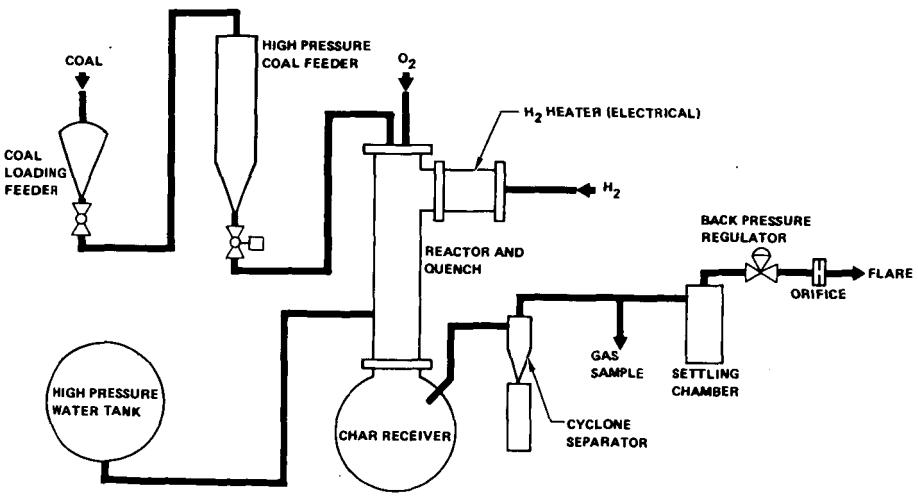

Figure 6. Flow Diagram of 0.2-tph Reactor Test System

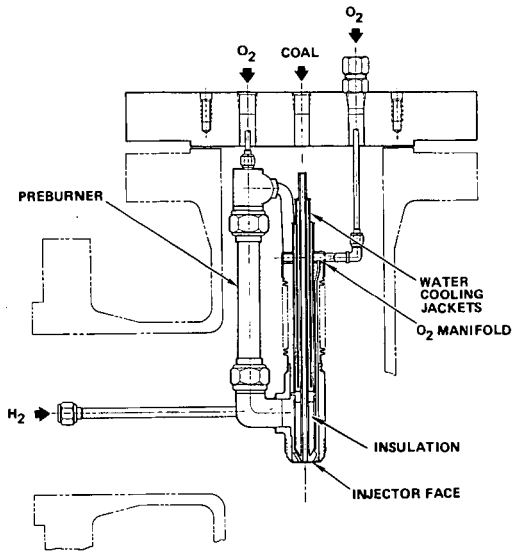

Figure 7. 0.2-tph 4-on-1 Injector and Preburner With Oxygen Injection Capability

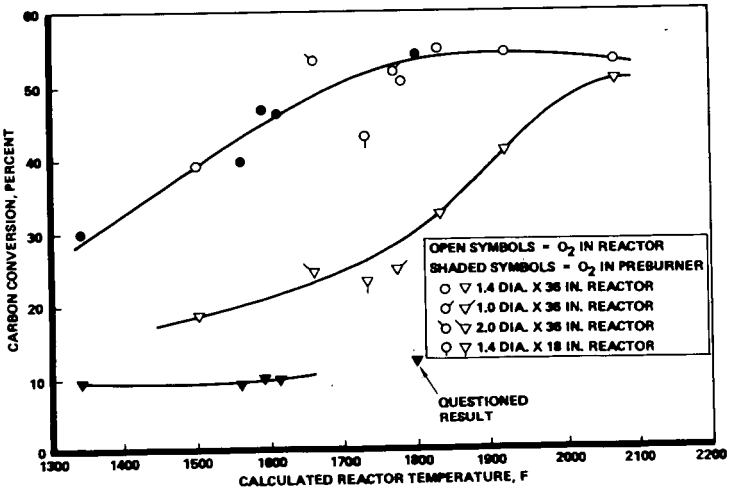

Figure 8. Carbon Conversion Results From 0.2-tph Reactor Testing

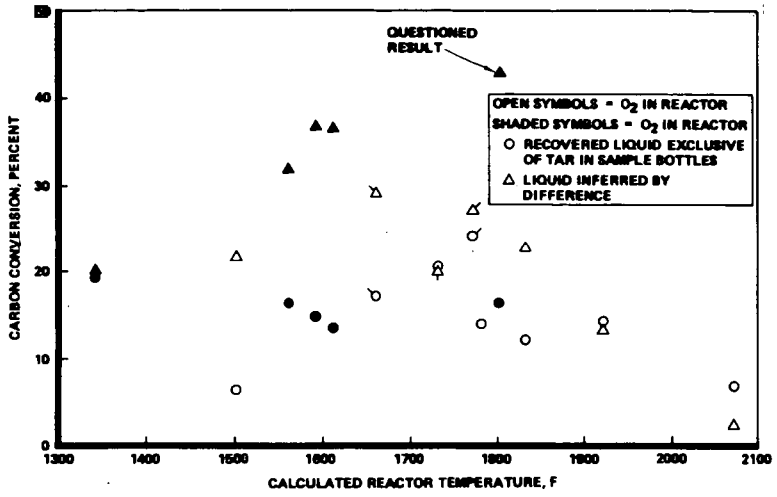

Figure 9. Carbon Conversion to Liquids From 0.2-tph Testing

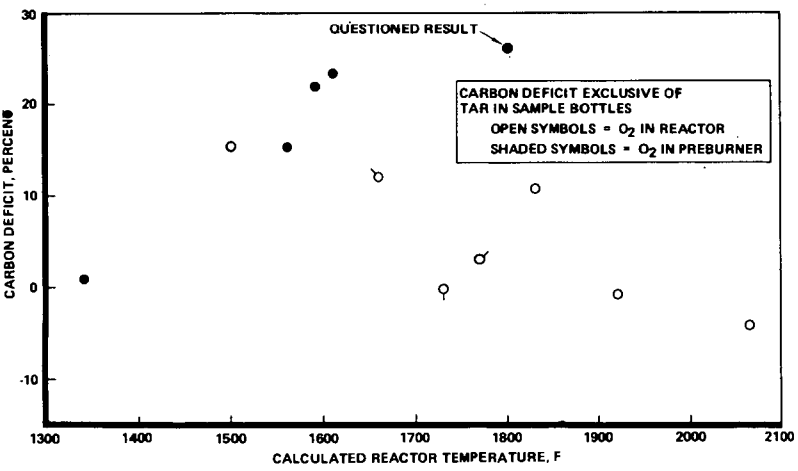

Figure 10. Carbon Deficit in Products From 0.2-tph Testing